V.B.15 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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Objectives

- Develop robust HPA immobilization strategies
- Develop a hybrid HPA polymer from HPA functionalized monomers for elevated temperature and drier fuel cell operation
- Fabricate mechanically robust membranes from HPA polymer suitable for use in proton exchange membrane (PEM) fuel cells

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(D) Thermal, Air and Water Management

Technical Targets

This project is developing new proton conducting membranes using HPA. These materials will meet the following DOE 2010 membranes for transportation applications targets:

- Proton Conductivity: >0.1 S cm^{-1} at ≤120°C and <1.5 kPa H_2O
- Durability: 5,000 h at ≤80°C, 2,000 h at >80°C
- Cost: <\$40 m^{-2}

Approach

Our approach is to use HPA, an inorganic super acid, as the acid functionality in a fuel cell proton exchange membrane. A number of HPAs have the highest recorded proton conductivity of any solid state material at room temperature, but are extremely water soluble. A vast synthetic methodology exists in the literature to fabricate hybrid HPA materials and polymers, but little of it is concerned with free acid HPA that would conduct protons. Much of this is based on lacunary HPA, Figure 1, in which 1, 2, or 3 metal octahedral are selectively removed from the HPA framework and the vacancies substituted with organic linkages that may be monomers suitable for polymerization.

We will initially determine which HPA linkage chemistry is the most stable in the fuel cell environment by fabricating phenyl derivatives of the various hybrid HPA and studying their decomposition, or lack of in

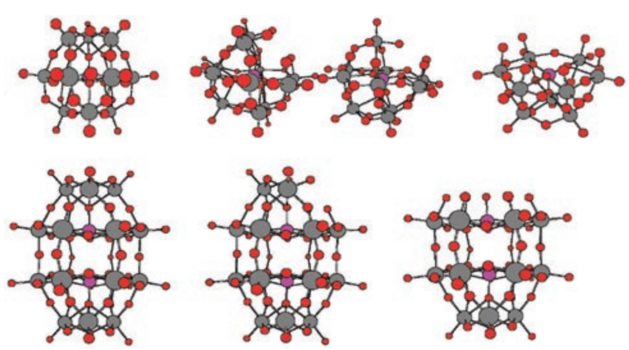

FIGURE 1. HPA Structures and Lacunary HPA based on them; top row Keggin structure, *e.g.* $[PW_{12}O_{40}]^{3-}$, bottom row, Dawson structure, e.g. $[P_2W_{18}O_{62}]^{6-}$

heated aqueous acid. We will also need to determine the most efficient method of fabricating free acids of HPA polymers. Proton conduction in these materials will be studied by electrochemical techniques and pulse field gradient spin echo (PFGSE) solid state nuclear magnetic resonance (NMR). The HPA polymers will be optimized for proton conduction at room temperature and then 120°C under dry conditions. We will fabricate films of the HPA polymers and optimize the mechanical properties of these films. The membranes will finally be optimized for durability and cost.

Accomplishments

This project has just been initiated and has no significant progress to report at this time.

FY 2006 Publications/Presentations

1. "Novel Approaches to Immobilized Heteropoly Acid Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes", A.M. Herring, poster presentation, presented at the U.S. DOE Hydrogen Program 2006 Annual Merit Review Meeting, Crystal City, VA, May 2006.